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THE STUDY OF TRANSPARENT PLASTICS USED AS LASER PROTECTION, (U)

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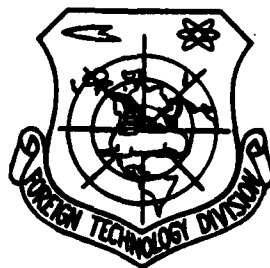
FOREIGN TECHNOLOGY DIVISION



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by

Hua Xiantong, Huang Meiyu, et al.



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AB

THE STUDY OF TRANSPARENT PLASTICS USED AS LASER PROTECTION

--Polymethylmethacrylate with an absorption wavelength of 5300Å

by Hua Xiantong (Hua Hsien-t'ung), Huang Meiyu (Huang Mei-yu),
Qian Chunqin (Ch'ien Ch'un-ch'in), and Pan Ang (P'an Ang)

ABSTRACT

We studied a successful absorption-type laser protective transparent plastic which has a dye as an additive. Its green light transmissivity is less than 0.1% for a wavelength of 5300Å. Under laser irradiation with an energy density of 190J/cm² (pulse width 80X10⁻⁹) it is still not penetrated or shattered. Under conditions of high brightness there is no effect on optical resolution. Tests were conducted on the eyes of domestic (angora white) rabbits and the protective effects were very good. After two months of natural atmospheric ageing no effect whatever was produced and it can be used as a laser protective material.

Laser protection involves physical safety of humans and mainly is preventing the eyes from being damaged by laser beams. The human eye reacts most sensitively to a green light wave range of approximately 5300Å and research into protection against this is of practical significance. Since 1965 many countries have been doing development work [1-6, 17, 18], and although people from many fields have studied this problem, up to now there are only two practical applications: one is the absorption type, i.e., optical filter glasses which absorb lasers and do not allow them to pass through; the other is the reflective type, i.e., a reflective layer coated on the glasses which reflects all or most of an injected laser, thus achieving a protective effect. But the disadvantages of the latter are that the specific

weight of existing materials is great, the technology is complicated, they are easily shattered, and the protective effects are limited by the injection angle of the light.

The requirements of transparent materials to serve as laser protection are: (1) it must filter out all or the most part of lasers in a narrow range of wavelengths; (2) except for the laser wavelengths which are absorbed it must pass visible light to the greatest extent, i.e., transparency must be high. Prior to 1969, all the filters used for absorption were inorganic glass, the lenses were thick, comparatively heavy, and easily shattered by a laser [7]; since 1970 a number of countries have done a great deal of development work in the field of the destructive effects of lasers on transparent plastics [4, 8-16], many used various additives as an absorptive material which was combined with polymethylmethacrylate, pulverized, injection molded, and made into a laser protective transparent material [4, 17]. Some thick cyclo organic compounds are mixed into the PMMA which when subjected to laser excitation can produce a three-fold state of absorption [18].

In order to have protective effects against a laser with a wavelength of 5300\AA and for comparing the advantages and disadvantages of the various materials and techniques, we selected an oil soluble product color dye having characteristic absorption peaks for use as the additive, after solution in a methylemethacrylate monomer, polymerization was accomplished and the results were very good. It has the highest absorption of green light at a wavelength of 5300\AA , all visible light of other wavelengths can pass as shown in Fig. 1.

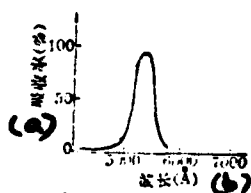


Fig. 1. Absorption of dye

KEY: (a) absorption rate (%); (b) wavelength (Å)

TEST RESULTS

1. Selective dyes and the preparation of organic glass

The solutions of various dyes, having absorption peaks in the range of 5100-5500Å as measured by a spectroscope, can all be given solubility tests in a monomer (Table 1); they can be dissolved in methylmethacrylate, and then polymerization is accomplished with no color fading at all and the pigmented organic glass lenses obtained can be used for protective eyewear.

(a) 染料名称 (商品名)	(b) 可见光吸收峰 (Å)	(c) 在甲基丙烯酸甲酯中的溶解性
(d) 橡胶红	5260	溶 (r)
(e) 蜡红	5150~5400	溶 ..
(f) 油溶红	5250~5320	溶 ..
(g) 西瑞斯红 2B (Ceres Red 2B)	5290	溶 ..
(h) 西瑞斯红 5B	5320~5350	溶 ..
(j) 西瑞斯红 7B	5350~5380	溶 ..
(k) 分散红	5320	溶 ..
(l) 三红 GFL	5100~5260	不溶 (s)
(m) 舍海莲红莲	5430~5350	溶 (r)
(n) 罗丹明 6G (Rhodamine 6G)	5320	较少 (t)
(o) 阿斯特拉宗红 (Astrazon Red)	5430	溶 (r) 70°C 以上褪色 (u)
(p) 卡宾紫 2R (Carbolan Violet 2R)	5430~6050	溶 (r)
(q) 艳红 ERLN	5180~5550	溶 ..

Table 1. The visible light absorption peaks of dyes and their solubility in methylmethacrylate

KEY: (a) dye name (commercial name); (b) visible light absorption peak (Å); (c) solubility in methylmethacrylate; (d) rubber red; (e) wax red; (f) oil soluble red; (g) Ceres red 2B; (h) Ceres red 5B; (j) Ceres red 7B; (k) disperse red; (l) jade red GFL; (m) semaron reddish violet; (n) Rhodamine 6G; (o) Astrazon Red; (p) Carbolan Violet 2R; (q) bright red ERLN; (r) soluble; (s) insoluble; (t) slightly soluble; (u) color fades above 70°C

2. Testing

(1) Laser absorption tests *

The light source used a Q-switching neodymium glass laser with a total energy of 1.5J, the wavelength was 1.06 μm, after passing through a lithium iodate frequency doubler a beam of 5300Å is irradiated, and the radiation time is 80 nanoseconds. The tests were

conducted using three types of energy density conditions:

(a) casual focusing, light spot diameter 2cm, energy density 0.477J/cm². Pulse width 80X10⁻⁹ seconds.

(b) focused 16 times, light spot diameter 5mm, energy density 7.63J/cm². Pulse width 80X10⁻⁹ seconds.

(c) focused 400 times, spot diameter 1mm, energy density 190.8J/cm². Pulse width 80X10⁻⁹ seconds.

Since the instruments were not sensitive enough we could only visually judge the conditions of green light transmission which were on each occasion simultaneously observed by 3-6 people. The test results are given in Tables 2 and 3.

(a) (商品名)	(b) (%)	(c) (毫米)	(d) 本 色 照 射		
			(e) 不聚焦, 能量密度为 0.477焦/厘米 ²	(f) 聚焦16倍, 能量密度为 7.63焦/厘米 ²	(g) 聚焦400倍, 能量密度为 190.8焦/厘米 ²
1. 蜡红 (h)	0.1	2.52	+	+	
	0.05	2.48	+	+	
2. 橡胶红 (j)	0.04	2.46	+		
	0.02	2.37	+		
3. 西德莱红 2B (k)	0.01	2.47	--		
	0.02	2.55	+	+	+
	0.04	2.60	+		
	0.06	2.55	+		
4. 西德莱红 5B (l)	0.01	2.38	-		
	0.02	2.52	+	+	+
	0.04	2.45	+		
	0.06	2.58	+		
5. 西德莱红 7B (m)	0.01	2.39	-		
	0.02	2.48	+	+	+
	0.03	2.26	+		
	0.04	2.45	+		

Table 2. Laser absorption tests (Red color dyes)

KEY: (a) dye (commercial name); (b) dye concentration (%); (c) PMMA thickness (mm); (d) laser irradiation; (e) unfocused, energy density 0.477J/cm²; (f) focused 16 times, energy density 7.63J/cm²; (g) focused 400 times, energy density 190.8J/cm²; (h) wax red; (j) rubber red; (k) Ceres red 2B; (l) Ceres Red 5B; (m) Ceres Red 7B.

NOTES: * The laser's total energy was 1.5J. In the table "+" means absorption results were good, "-" means absorption was incomplete and there was laser penetration.

** One time irradiation produced damaged spots.

(a) (商品名)	(b) (%)	(c) (毫米)	(d) (未聚焦)	(e) (聚焦16倍)	(f) (聚焦400倍)
(g) 分散红 FB	0.15 (饱和)	2.43	+	+	+
(h) 亮红 ERLN	0.15	2.55	-	-	-
	0.10	2.55	-	-	-
	0.05	2.47	-	-	-

Table 3. Laser absorption tests (Product color dyes)

KEY: (a) dye (commercial name); (b) dye concentration (%); (c) PMMA thickness (mm); (d) unfocused, energy density 0.477J/cm²; (e) focused 16 times, energy density 7.63J/cm²; (f) focused 400 times, energy density 190.8J/cm²; (g) disperse red FB; (h) bright red ERLN; (j) (saturated).

NOTES: * The laser's total energy is 1.5J, pulse width 80X10⁻⁹s. In the table "+" means absorption results were good, "-" means absorption was incomplete and there was laser penetration.

** One time irradiation produced damaged spots.

(2) Optical density tests

A well prepared strip of PMMA was placed on a Unicam SP-700 model ultraviolet and visible light spectroscope and tested. The results are shown in Table 4. The results were that the product color dye "Disperse Red FB" had an optical density greater than 3 in the 4900-5560 wavelength range and the red color dye "Ceres Red 5B" had an optical density greater than 3 in the 4020-5290 wavelength range.

(a) 样品编号	(b) 样品厚 (毫米)	(c) 波长 (埃)	(d) 透射率 (%)	(e) 光密度 ($D = \log \frac{1}{T}$)
FB-01 (分散红 FB, 0.1%) (f)	2.43	4080	45.0	0.347
		4650	1.0	2.0
		4900	<0.1	>3.0
		5260	<0.1	>3.0
		5560	0.1	3.0
SP-002 (西尔赤红 5B, 0.1%) (g)	2.52	4020	<0.1	>3
		5100	<0.1	>3
		5290	0.1	3.0
		>5290	70	

Table 4. Optical density testing

KEY: (a) Designation of specimen; (b) specimen thickness (mm); (c) wavelength (Å); (d) transmissivity (%); (e) optical density; (f) Disperse Red; (g) Ceres Red 5B

3. Atmospheric Ageing

A glass plate which is up to the required standards is divided into two pieces, one piece is placed outdoors and exposed to sunlight, wind and rain for two months. It is then compared with the other specimen which has been kept in a dark place indoors. The results are:

1. The surface of the specimen which has been aged was not damaged nor does the glass sheet show silver grain phenomenon.

2. The visible light absorption pattern shows that no change occurs in the position of the absorption peak which is still about 5300\AA except that after ageing the absorption peak became slightly narrower (see Fig. 2).

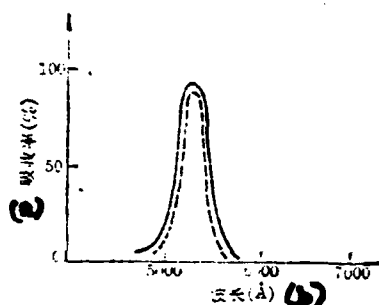


Fig. 2. Comparison of visible light absorption before and after ageing.

———— specimen which has not been aged
----- aged specimen

KEY: (a) absorption rate (%); (b) wavelength (\AA)

4. Measurement of optical resolution*

Since the red dye transparency and the absorption peak position were not ideal, we selected product color dyed plastic protective lenses of two thicknesses and conducted optical resolution measurements. It is hoped that it is understood that these are not suitable for use as protective lenses. The results of the measurements are shown in Table 5. Also we compared the results of the measurements with that of inorganic glass protective lenses (see Table 6). The

* Lab 5 of the Institute of Chemistry, Chinese Academy of Sciences, assisted in the measurements.

results of the measurements show:

(1) at high brightness (over 50 lux, corresponding to conditions of a clear day indoors) resolution was comparable to that of not wearing glasses.

(2) at low brightness (at 0.02 lux, corresponding to conditions approaching darkness) the resolutions were somewhat different.

(3) compared to inorganic glass protective glasses, under conditions of low brightness, resolution differed by about half an order.

(a) 观察者	(b) 低亮度下 (0.02 lux)			(c) 高亮度下 (50 lux)		
	(d) 正常分辨率			(e) 戴眼镜分辨率		
	(f) 2.52mm	(g) 3.3mm	(h) 正常分辨率	(j) 2.52mm	(k) 3.3mm	(l) 正常分辨率
1.	1.1	1.0	1.0	1.1	1.1	1.1
2.	1.1	0.9	0.9	1.1	1.1	1.1
3.	1.2	1.1	1.0	1.2	1.2	1.2
4.	1.2	1.0	1.0	1.2	1.2	1.2
5.	1.2	1.1	1.0	1.2	1.2	1.2
(m) 平均值	1.15	1.02	0.98	1.16	1.16	1.16

Table 5. The effects on optical resolution of protective glasses of different thicknesses and at different brightnesses (Note 1).

NOTES: (1) Resolution was based on the criteria of the "Letter E" vision chart. Eye to Letter E distance was 64cm.

(2) Observed under low brightness background light of 0.02 lux.

(3) Observed under high brightness background light of over 50 lux.

(4) Normal resolution is divided into grades of 0.1 to 1.2; 0.1 corresponds to 0.1 of the ophthalmology vision chart criteria; 1.2 corresponds to 1.5 of the ophthalmology vision chart criteria.

KEY: (a) Observer; (b) under low brightness (Note 2); (c) under high brightness (Note 3); (d) Normal resolution (Note 4); (e) resolution wearing glasses; (f) lens thickness 2.52mm; (g) lens thickness 3.3mm; (h) normal resolution (Note 4); (j) resolution wearing glasses; (k) lens thickness 2.52mm; (l) lens thickness 3.3mm; (m) mean value.

(a) 序 号	(b) 无 色 玻 璃			(c) 有 色 玻 璃		
	(d) 无 色 玻 璃			(e) 有 色 玻 璃		
	(f)	(g)	(h)	(i)	(j)	(k)
1.	1.0	0.7	0.7	1.2	1.0	0.9
2.	1.2	0.9	0.8	1.2	1.2	1.0
3.	1.2	0.9	0.8	1.2	1.0	0.9
4.	1.0	0.8	0.7	1.2	1.0	1.0
5.	1.2	0.9	0.8	1.0	1.0	1.0
6.	1.0	0.7	0.7	1.2	1.0	1.0
(m)	1.1	0.81	0.73	1.16	1.02	0.94

Table 6. The effects on optical resolution of two different types of protective glasses (inorganic glass and plastic) under different brightnesses (Note 1).

NOTES: (1), (2), (3), (4) same as for Table 5.

KEYS: (a), (b), (c), (d), (e), (h), (j), (m) same as Table 5;
(f), (k) inorganic lens; (g), (l) plastic lens.

5. Biological appraisal**

The appraisal used a YAG-Nd frequency doubler Q-switching pulse laser at a wavelength of 5300Å; the appraisal was accomplished for two types of protective glasses. Their specifications were thick lenses of 3.3mm and thin lenses of 2.52mm.

The eyes of domestic (angora white) rabbits were subjected to an energy density of 103mJ/cm² at a power density of 10.3MW/cm² without the protective lenses, which resulted in severe bleeding of the retina and hyaloid body. After laser irradiation in 30 spots with the use of the protective lenses (both thick and thin type) close observation revealed no visible damage on the retina.

The threshold value (minimum value) for visible damage to the rabbits' cornea was 1.6mJ/cm².

** Biological appraisal was carried out with the assistance of Lab 5, Laser Biological Effects Dept., Biophysics Institute, Chinese Academy of Sciences.

CONCLUSIONS

1. The results obtained from the conducted tests show that laser protective material made of transparent plastic can be of practical use and its strong points are:

(1) The density of plastic is low, about half that of inorganic glass. For example the density of PMMA is 1.19g/cm^3 while that of inorganic eyeglasses glass is as much as $2.25\text{-}4.0\text{g/cm}^3$.

(2) The impact resistance and shockproof properties of plastics are better than that of glass. Upon direct laser irradiation at 70J/cm^2 ^{inorganic glass} can be shattered, while upon laser irradiation at 190J/cm^2 organic glass is still not shattered.

(3) According to the usage requirements in plastics, adding absorbents possessing various characteristic absorption peaks can achieve protective effects.

(4) The protective effects of plastics are not affected by the laser injection angle.

2. The selection of dyes

(1) Since we did not use the plastic injection techniques normally used in the biographic literature but used the technique of dissolving the dye in a monomer and then carrying out polymerization, therefore it was necessary that the dyes have a definite solubility in methylmethacrylate and at the same time not fade during the monomer-polymer process. Many of the red color and product color dyes in Table 1 satisfy this condition.

(2) The laser absorption effects for a wavelength of 5300\AA were good ^{for 0.02%} ~~that of red color dyes~~ ^{and for 0.15%} ~~was 0.02%, of~~ product color dyes ~~0.15%~~. They can completely satisfy this condition of absorption.

(3) In regard to the effect of transparency and optical resolution, the effect of red color dyes was greater than that of product color dyes.

(4) From an upper to lower limit with a light density of greater than 3 we can see that:

red color dyes: $4020\text{-}5300\text{\AA}$

product color dyes: $4650\text{-}5560\text{\AA}$.

Combining the above four points, protection against green light at a wavelength of 5300\AA by product color dyes is best.

3. From the effects on optical resolution it can be seen that under conditions of low brightness plastic protective material is half a grade lower than inorganic glass protective lens material.

4. From the appraisal results of biological tests conducted on domestic rabbits it can be seen that using these types of materials would be effective for protecting the human eye from green light of 5300Å.

5. The results of atmospheric ageing show that these types of materials can be used continuously outdoors for over 2 months at least. The properties of lenses placed indoors for 5 years did not change and thus they can be used indoors for over 5 years.

6. In the future we should continue to develop transparent plastics made with dyes soluble in monomers and polymers, and to conduct protection research work for various lasers of different wavelengths in order to guarantee the safety of personnel in laser research as well as personnel who use laser equipment.

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